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(54) **Process for granulating additives for organic polymers.**

(57) Described is a process for granulating powdery organic and inorganic antiacid additives which is carried out in the presence of tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane in the molten state.

EP 0 514 784 A1

The present invention relates to a process for granulating powdered additives for organic polymers.

More in particular, the present invention relates to a process for granulating powders of organic and inorganic antiacid additives, together with an antioxidant stabilizer, i.e., tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyloxymethyl]-methane.

Organic polymers, in particular polyolefins, require the addition of additives suitable for neutralizing the acidic residues deriving from the polymerization catalysts during their processing. They furthermore require the addition of stabilizers against the oxidative degradation caused by light and/or heat.

One class of antioxidant additives are the sterically hindered phenols, such as tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane.

Both the antiacid additives and tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane usually are in powder form.

When said powders are used during the processing of the polymers, they display the drawback of showing a tendency to disperse in air, thereby causing damage to the health of the operators and creating safety risks due to the possibility of explosions.

Another disadvantage associated with the use of these additives in powdery form is their tendency to agglomerate inside the feed hoppers, resulting in an uneven metering of the additives to the polymers to be compounded.

On the other hand, the use of antiacid additives and tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane in the stabilization or organic polymers poses difficulties as regards the obtainment of a complete homogenization of the mixtures of said additives and, consequently, of their mixtures with the organic polymer. This results in an ununiform stabilization.

In order to overcome the above drawbacks, attempts have been made in the past to granulate these additive powders, either as individual compounds or as blends thereof, so as to obtain granulates which can easily be handled and metered.

For that purpose, granulation systems have been resorted to which use dry-compacting machines or dry pelletizers. Unfortunately, in most cases, these procedures proved to be poorly effective, because the resulting granules showed a low mechanical strength and were difficult to handle, owing to their tendency to crumble.

As an alternative, binding agents can be used, such as waxes, paraffins, stearic acid amides, etc. However, in that case undesired components are added to the polymer.

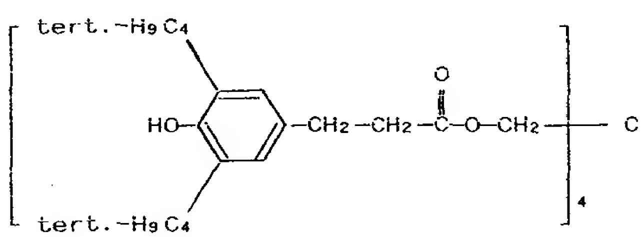
It has now been found that the drawbacks of the prior art processes can be avoided by means of an improved granulation process which affords granules with improved mechanical strength without making necessary the addition of foreign compounds to the stabilizer formulation.

Furthermore, said process makes it possible to obtain granules of the above stabilizer compositions which display a high level of homogeneity.

Therefore, the present invention provides a process for granulating powdery organic and inorganic antiacid additives for polymers and/or tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyloxymethyl]-methane by using pressure and/or heat, wherein said granulation is carried out in the presence of at least 1% by weight of said tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane in the molten state, homogeneously distributed throughout the powder mass.

Usually the amount of molten tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane is at least equal to 5% by weight and preferably at least 10% by weight, based on the weight of the powder (mixture) to be granulated.

Tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane has the formula:



and is used in the art for the stabilization of organic polymers, as disclosed, e.g., in US-A-3,644,428.

Said compound can exist as crystalline solid in various allotropic forms showing melting temperatures

within the approximate range of from 110° C to 125° C.

Besides the above crystalline forms, said compound can also exist in an amorphous form, as disclosed in US-A-4,886,900, having a glass transition temperature (T_g) within the range of from 40° C to 54° C and not showing any endothermal melting peaks within the temperature range of from about 50° C to 200° C. This amorphous form may be obtained, according to said patent, by rapid cooling of the molten compound.

According to one preferred embodiment of the process of the present invention, tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane is contained in the powder to be granulated in its amorphous form, in an amount which is at least equal to the weight percentage thereof which is required to be present in the molten state.

Thus, by operating at temperatures which are higher than the T_g of amorphous tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane, but lower than the melting temperatures of the compound in its crystalline forms, said compound will be found in practically unchanged form in the granulated product.

In this case, the granulation of the powders can be carried out by means of a roller compacting machine, with rollers heated at the required temperature.

More advantageously, one can use a single-screw or double-screw extruder with zones heated at suitable temperatures, so as to produce continuous strands which can subsequently be cut. In that way, granules of different sizes can be obtained, depending on the diameter of the extrusion die.

In the case in which, on the contrary, exclusively crystalline tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane is used,the present process is preferably carried out at temperatures of about 110° C to 125° C and with contact times such that at least that amount of said compound is in the molten state which is required for said process.

The amount of tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane to be employed preferably ranges from 10 to 90% by weight, based on the total amount of powder (mixture) to be granulated.

The conventionally used antiacid additives are (metal) stearates, such as, e.g., calcium, zinc, magnesium and aluminium stearates; oxides, such as zinc and magnesium oxides; titanium dioxide; and synthetic or natural carbonates, such as calcium carbonate and hydrotalcite.

The above compounds are well known and commercially available. In particular, as regards hydrotalcite, a compound having the formula

$Mg_6Al_2(OH)_{16}(CO_3)*4H_2O$,

a product marketed by the company KYOWA under the trade name DHT4A may, for instance, be employed.

As amorpous tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane, a product which is marketed by Enichem Synthesis under the trade name Anox® 20 AM can, for example, be used.

Examples of commercially available crystalline tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane are the products Anox® 20 (Enichem Synthesis) and Irganox® 1010 (Ciba-Geigy).

The granules obtained by means of the process according to the present invention show a satisfactory mechanical strength. Anyway, the small amounts of powders which may be formed when exerting mechanical stress, are free-flowing and dust-free. Therefore the above products can homogeneously be metered into the polymer.

Furthermore, by properly selecting the relative amounts of powders, granules can be prepared which contain the antiacid additives and the antioxidant in the desired amounts and with a high level of homogeneity. Thus an extremely homogeneous distribution of the above additives throughout the polymer to be stabilized may be obtained without the need of introducing undesired compounds. Moreover, a dust-free operation is possible thereby.

The following examples are given for merely illustrative, non-limitative purposes.

EXAMPLE 1

100 g of ANOX® 20 and 100 g of calcium stearate were charged to a planetary powder mixer. The homogenized mixture was fed to a BRABENDER extruder (screw length 475 mm, screw diameter 19 mm) with a compression ratio of 1:4 and four screw heating zones (optionally thermostatable at four different temperatures). The mixture was extruded through a circular die (diameter 25 mm) at a screw speed of 70 rpm and a constant temperature of 115° C.

A strand was obtained, which, after cooling down to room temperature was cut in order to obtain

granules of approximately 2.5 mm in size.

The X-ray diffraction spectra of the granules showed that the latter were homogeneous and constituted by calcium stearate and tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane in both amorphous and crystalline forms, with the crystalline form prevailing over the amorphous form. The product was dust-free.

EXAMPLE 2

100 g of previously ground ANOX® 20 AM and 100 g of calcium stearate were charged to a planetary powder mixer. The homogenized mixture was treated as described in example 1, with the only difference that the temperature was kept constant at 100 °C.
The product obtained was composed of calcium stearate and amorphous tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane.

EXAMPLE 3

100 g of ANOX® 20, 20 g of previously ground ANOX® 20 AM and 100 g of calcium stearate were charged to a planetary powder mixer. The homogenized mixture was treated as described in example 2.
Obtained was a product which was analogous to the product obtained in example 1.

EXAMPLE 4

160 g of ANOX® 20 and 40 g of zinc stearate were charged to a planetary powder mixer. The homogenized mixture was treated as in example 1, with the only difference that the temperature of the extruder was adjusted at 110 °C.

Obtained was a homogeneous product composed of zinc stearate and both amorphous and crystalline tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane, with the crystalline form prevailing over the amorphous form. The product was dust-free.

EXAMPLE 5

80 g of ANOX® 20, 80 g of calcium stearate and 40 g of zinc stearate were charged to a planetary powder mixer. The homogenized mixture was treated as described in example 1, with the only difference that the temperature profile of the extruder, from the feeding zone to the head zone, was 110 °C, 110 °C, 110 °C and 115 °C.

Obtained was a homogeneous product composed of calcium stearate, zinc stearate and both amorphous and crystalline tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane, with the crystalline form prevailing over the amorphous form. The product was dust-free.

EXAMPLE 6

100 g of ANOX® 20, and 100 g of zinc oxide were charged to a planetary powder mixer. The homogenized mixture was treated as described in example 1.

Obtained was a product composed of a homogeneous mixture of zinc oxide and both amorphous and crystalline tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane, with the crystalline form prevailing over the amorphous form. The product was dust-free.

EXAMPLE 7

100 g of ANOX® 20, and 100 g of hydrotalcite were charged to a planetary powder mixer. The homogenized mixture was treated as described in example 4.

Obtained was a product composed of a homogeneous mixture of hydrotalcite and both amorphous and crystalline tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane, with the crystalline form prevailing over the amorphous form. The product was dust-free.

EXAMPLE 8

180 g of ANOX® 20 and 20 g of previously ground ANOX® 20 AM were charged to a planetary powder

mixer. The homogenized mixture was treated as described in example 2.

Obtained was a product composed of a homogeneous mixture of amorphous and crystalline tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane, with the crystalline form prevailing over the amorphous form. The product was dust-free.

EXAMPLE 9

160 g of ANOX® 20 and 40 g of previously ground ANOX® 20 AM were charged to a planetary powder mixer. The homogenized mixture was treated as described in example 2.
Obtained was a product analogous to the product of example 8.

EXAMPLE 10

200 g of ANOX® 20 were charged to a planetary powder mixer. The homogenized sample was treated as described in example 1, with the only difference that the temperature profile of the extruder, from the feeding zone to the head zone, was 110 °C, 110 °C, 110 °C and 112 °C.
Obtained was a product analogous to the product of example 8.

EXAMPLE 11

In order to compare the mechanical properties of granules obtained according to the process of the present invention to those of products obtained by powder compaction, tests of crumbling resistance were carried out.

A machine for powder sieving ("Pulverisette" manufactured by the company FRITSCH, FRG) was used. This machine was equipped with five sieves of decreasing mesh size, from the top downward 2.80, 1.70, 1.00, 0.50 and 0.18 mm, and with a cover and a collecting bottom tray.

The machine performed the sieving operation by causing the sieve stack to vibrate. The vertical vibration stroke was 1.6 mm.

In order to cause the granules to undergo percussions, the sieving was carried out by charging to the first four sieves glass balls (diameter 17.3 mm, average weight 6.5 g). The number of balls charged to the sieves was: 11 balls to the first sieve (i.e., the 2.80 mm sieve), 10 balls to the second sieve (1.70 mm), 9 balls to the third sieve (1.00 mm) and 8 balls to the fourth sieve (0.50 mm).

The above test was carried out on samples obtained form examples 4, 5, 7 and 10 and additionally on a sample obtained by means of the compaction of powders of ANOX® 20 and zinc stearate (ratio 4:1, Product "A") and on a sample obtained by means of the compaction of ANOX® 20 powder (Product "B").

For each sample, 100 g of product were dry-sieved for 5 minutes, in the absence of glass balls, in order to determine the initial granulometric distribution. Then the balls were charged to the sieves and the determination of granulometric distribution was repeated after a 10- and 20-minutes sieving, respectively. The results are reported in Table I below.

From an examination of the results obtained it is evident that the products prepared by means of the process according to the present invention are endowed with a higher mechanical crumbling resistance than those obtained by compacting the powders. In fact, with the mechanical stress conditions being the same, the products according to the present invention give rise to a decidedly smaller amount of fine fractions ("dust").

EXAMPLE 12

By using a powder planetary mixer, a sample of commercial polypropylene (type MOPLEN® FLF20) admixed with 0.2% by weight of a mixture of ANOX® 20 and calcium stearate powders (ratio 1:1), analogous to that used in example 1, was prepared.

By operating according to the same procedure, a sample of the same polymer, admixed with 0.2% by weight of granules obtained from example 1, previously ground, was prepared.

The resulting samples were subjected to repeated extrusion through a BRABENDER type laboratory extruder, at a screw speed of 50 rpm and a temperature profile of 190 °C, 235 °C, 270 °C and 270 °C.

In Table II below the Yellowing Index (YI) and the Melt Flow Index (MFI) of both polymer samples are reported, which were measured after the first, the third and the fifth extrusion runs. It can be observed that the granulation of the additives by means of the process according to the present invention is substantially immaterial as regards the performance thereof.

EXAMPLE 13

By operating in accordance with example 12, a sample of commercial polypropylene (MOPLEN® FLF20) admixed with 0.1% by weight of ANOX® 20 powder, analogous to those used in example 10, and a sample of the same polymer admixed with the same amount of granules from example 10, previously ground, were extruded.

The YI and MFI values of both polymer samples, as measured after the first, the third and the fifth extrusion run are reported in Table III below. As in example 12, the granulation of the additives had no influence on their performance.

Table I

		<0.18	0.18-0.5	0.5 -1.0	1.0 -1.7	1.7 -2.8	>2.8
Example 4	0 minutes	--	1.2	6.0	49.1	39.9	3.8
	10 minutes	2.5	15.1	13.0	39.2	30.0	0.2
	20 minutes	3.8	31.7	14.2	30.1	20.2	--
Example 5	0 minutes	--	1.4	13.6	32.0	51.9	1.1
	10 minutes	2.1	10.0	17.9	27.5	42.5	--
	20 minutes	4.6	25.6	29.7	15.0	25.1	--
Example 7	0 minutes	0.3	0.6	2.0	43.7	53.4	--
	10 minutes	2.7	18.0	23.3	41.9	14.1	--
	20 minutes	5.4	30.9	34.7	26.7	2.3	--
Example 10	0 minutes	--	1.0	1.2	31.5	65.4	0.9
	10 minutes	1.8	8.2	10.0	25.1	54.9	--
	20 minutes	4.3	21.2	35.7	17.3	21.5	--
A	0 minutes	0.9	1.9	18.8	43.3	35.1	--
	10 minutes	21.4	69.2	9.4	--	--	--
	20 minutes	24.5	72.1	3.4	--	--	--
B	0 minutes	2.7	11.7	20.2	50.0	15.4	--
	10 minutes	6.1	30.2	27.5	35.6	0.6	--
	20 minutes	11.0	42.2	31.5	14.8	0.5	--

TABLE II

	Powders	Granules
YI - 1st extrusion	-2.5	-2.6
YI - 3rd extrusion	-0.8	-1.3
YI - 5th extrusion	0.7	0.3
MFI - 1st extrusion	20.7	20.6
MFI - 3rd extrusion	29.0	28.8
MFG - 5th extrusion	36.0	36.0

TABLE III

	Powders	Granules
YI - 1st extrusion	-1.8	-1.6
YI - 3rd extrusion	2.2	2.9
YI - 5th extrusion	5.9	5.7
MFI - 1st extrusion	15.7	15.5
MFI - 3rd extrusion	19.0	18.4
MFI - 5th extrusion	23.0	22.2

Claims

1. Process for granulating organic and inorganic antiacid additives for polymers and/or tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane by using pressure and/or heat, in which the granulation is carried out in the presence of at least 1% by weight of said tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane in the molten state.

2. Process according to claim 1, in which at least 5, and particularly at least 10% by weight of molten tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane are employed.

3. Process according to any one of claims 1 and 2, in which tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane is initially employed in amorphous form and in an amount at least equal to the weight percentage required to be in the molten state, and the process is carried out at a temperature higher than the glass transition temperature (T_g) of said amorphous form but lower than the melting temperature of said compound in crystalline form and under conditions in which at least the required amount of said molten compound is present.

4. Process according to any one of claims 1 and 2, in which all of the tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane is initially employed in one or more of its crystalline forms, and the process is carried out at a temperature of about 110 to 125°C and under conditions in which at least the required amount of said molten compound is present.

5. Process according to any one of claims 1 to 4, in which the granulation is effected by means of an extruder.

6. Process according to any one of claims 1 to 5, in which the antiacid additive is selected from metal stearates, oxides, carbonates and mixtures thereof.

7. Granular forms of organic and inorganic antiacid additives for polymers and/or of tetrakis-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionyl-oxymethyl]-methane, obtainable by the process of any one of claims 1 to 6.

8. Use of the granular forms according to claim 7 in the stabilization of organic polymers.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 8230

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 255 743 (ENICHEM SINTESI S.P.A.)	1-2,4,7, 8	C08K5/13 C08J3/22
D	& US-A-4 886 900 * page 3, line 4 - line 16 * * page 4, line 5 - line 7; claims 3-7; examples *		
X	CHEMICAL ABSTRACTS, vol. 106, no. 10, 9 March 1987, Columbus, Ohio, US; abstract no. 68211G, L.V. GLUSHKOVA ET AL.: 'Phase states of Fenozan 23 and its preparation in a dust-free final form' page 39 ; * abstract *	1-2,4, 7-8	
A	EP-A-0 392 392 (CIBA-GEIGY AG) * page 3, line 10 - line 20 * * page 12, line 13 - line 21; claims 1,6,7,14; example 1V *	1-2,4-8	
A	EP-A-0 278 579 (ENICHEM SYNTHESIS S.P.A.) * claims 1,7-10; examples *	1-3,7-8	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C08K C08J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	01 SEPTEMBER 1992	FUHR C.K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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